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SINTERING AND PROPERTIES OF Si_3N_4 WITH AND WITHOUT ADDITIVES BY HIP TREATMENT

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16. Abstract

HIP of Si_3N_4 powders with and without additives was performed using a glass container, and various kinds of pressureless-sintered Si_3N_4 were HIP'ed without a container. The effects of HIP treatment on density, microstructurem flexural strength, microhardness and fracture toughness on Si_3N_4 ceramics were studied. Using a glass container it was difficult ot reach theoretical density. The microhardness of HIP'ed Si_3N_4 without additives was low, and the fracture toughness of HIP'ed Si_3N_4 with and without additives was 22-25 W/m-K, and it decreased with increasing the amount of additives. The density, flexural strength and hardness of pressureless-sintered Si_3N_4 which contained Al_2O and Y_2O_3 as oxide additives were remarkably improved by HIP treatment using nitrogen as a pressure transmitting gas. It is very important to select the sintering conditions for fabricating the presintered body of Si_3N_4 in order to improve the mechanical properties of Si_3N_4 ceramics by HIP treatment. (Author)

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SINTERING AND PROPERTIES OF Si_3N_4 WITH AND WITHOUT ADDITIVES BY HIP TREATMENT

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1 Introduction /1372*

A great deal of research and development is being performed in relation with silicon nitride (Si_3N_4) ceramics as high-temperature strength materials, as in components for gas turbines and diesel engines, but since the covalence is strong and the self-diffusion coefficient of the structural atoms is extremely low [1] in these materials, it is commonly known that they possess very troublesome sintering properties [2]. Therefore, the manufacture [3] of these types of high-density sintered bodies has generally been performed by hot-press sintering, pressureless sintering, reaction sintering and CVD using small amounts of sintering additives (MgO, Al_2O_3, Y_2O_3, etc.), but each of these sintering methods also have various advantages and disadvantages.

However, reports of applications of hot isostatic press (HIP) technology to the sintering of Si_3N_4 ceramics have recently been announced one after the other accompanying improvements in the performance of the HIP equipment. For instance, Yamada, et al. [4] are reporting a correlation between phase transition in

* Numbers in the margin indicate pagination in the foreign text.

the HIP sintering of Si_3N_4 powders, using glass containers, with and without additives and their resultant densities. Meanwhile, Honma, et al. [5][6] are conducting investigations into sintering conditions and HIP conditions for Si_3N_4 by performing direct HIP treatment on pre-sintered bodies which were manufactured by hot press and pressureless sintering methods, without using containers.

This article is a report of the results of the HIP treatment of Si_3N_4 powder with and without additives using a glass container and the performance of direct HIP treatment on Si_3N_4 pre-sintered bodies manufactured by pressureless sintering, as well as the results of the measurement of the mechanical and thermal properties of, and studies on the influence of additives and the effects of HIP on, the resultant sintered bodies.

2 Methodology

2.1 Starting Base Materials

The powder characteristics of the 3 types of starting base materials of the Si_3N_4 used in this testing are shown in Table I. SN-A and SN-B were both manufactured by the nitrification of metallic silicon, while SN-C was manufactured by the gas phase method. Two types of compounds, $MgAl_2O_4$-Y_2O_3 and Al_2O_3-Y_2O_3, /1373

Table I. Characteristics of Si_3N_4 powders.

Powder	Phase (wt%)		Content of elements (wt%)							Specific surface area (m^2/g)
	α	β	N	O	C	Al	Ca	Mg	Fe	
SN-A	96	4	38.2	1.1	0.48	0.09	0.04	—	0.03	8.3
SN-B	92	8	38.4	—	—	0.25	0.24	<0.01	0.39	8.7
SN-C	90	10	38.7	—	—	<0.01	<0.01	<0.01	<0.01	10.0

were used as sintering additives.

2.2 Manufacture of Glass-encapsulated Materials and Presintered Bodies for HIP Treatment

The powders SN-A and SN-C were manufactured by themselves, or after having equal portions of $MgAl_2O_4$ and Y_2O_3 mixed with them as sintering additives, under conditions of room temperature-300 MPa, into 7^{ϕ} x 3^{t}mm pellets, heat treated at 1200°C in a nitrogen gas flow, and then packed into BN capsules. These BN-encapsulated samples were then each wrapped in a sheet of molybdenum (0.5 mm) and inserted into a pyrex tube (interior diameter 11 mm), which was then vacuum sealed.

Meanwhile, pre-sintered samples were manufactured by adding appropriate amounts of $MgAl_2O_4$-Y_2O_3 and Al_2O_3-Y_2O_3 to each of the starting powders SN-B and SN-C as sintering additives, as shown in Table II, and mixing the powders in an alumina pot, then casting the powders into 5mm x 6mm x 48mm samples, and finally, pressureless sintering the samples for several hours at 1750°C in N_2 gas. The dimensions of the pre-sintered samples after sintering were 4mm x 5mm x 39mm.

Table II. Starting powders of pressure-less sintered Si_3N_4.

	Powder	Additive
SSN 1	SN-B	Al_2O_3, Y_2O_3
SSN 2	SN-B	$MgAl_2O_4$, Y_2O_3
SSN 3	SN-C	Al_2O_3, Y_2O_3
SSN 4	SN-C	$MgAl_2O_4$, Y_2O_3

2.3 HIP Treatment

A high-temperature, small-scale HIP device manufactured by the Kōbe Seikōjo Co., Ltd. was used in this HIP treatment. The hot zone of this HIP equipment is shown in Figure 1. The dimensions of the treatment chamber were 100^{ϕ}mm x 130^{L}mm and W-Re was used as a thermocouple.

In the case of the HIP treatment of the glass-encapsulated materials, the encapsulated material was placed in the center of the hot zone of the HIP equipment, surrounded by BN powder which filled a carbon crucible, and treated at 1450 to 1700°C under 100 to 150 MPa pressure, using Ar gas as a pressure-transmitting medium. The rate of temperature increase and decrease in this case was approximately 1000°C/hr.

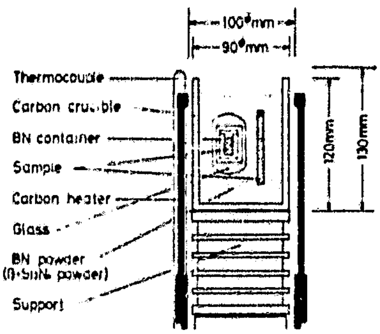

Fig. 1. Hot zone of HIP equipment.

While, in the case of the HIP treatment of the pre-sintered samples, treatment was performed at 1700°C, 120 MPa, for 60 minutes, using Ar and N_2 gas as pressure-transmitting media. In these instances, the void surrounding the pre-sintered sample was filled with beta-Si_3N_4 and BN powders in order to prevent the pre-sintered sample and the carbon crucible from coming in contact with each other. The rates of temperature increase and decrease used in these cases were approximately 1000°C/hr and 500°C/hr.

2.4 Density Measurement, Crystal Phase Establishment, and Scanning Electron Microscope Observations

After removing foreign substances from, and then polishing, the surfaces of the resultant materials, the relative density of the materials was measured using Archimedes' method. The crystal phase of these materials was also established by X-ray diffraction analysis using Cu-K alpha rays [7]. Furthermore, gold deposition was performed on the fracture surfaces of the materials in conjunction with SEM observation.

2.5 Flexural Testing

Flexural testing was performed on the pre-sintered samples and subsequent HIP treated materials, using a 3-point bending method at room temperature on 30mm span-lengths of material. The cross-head rate during testing was 0.5mm/min. The samples used for this flexural testing were "freshly sintered', without having been polished or finished in any way.

2.6 Thermal Conductivity Measurement

Thermal conductivity was determined by the laser flash method [8], using a TC-3000-H Thermal Coefficient Measurement Device manufactured by the Shinkū Kōri Co., Ltd. Both surfaces of the samples were mirror finished with diamond paste until parallel and graphite was applied to one of the surfaces, while a thermocouple, for the detection of thermoelectromotive force, was affixed to the other surface with Ag paste. The measurement was then performed by first heating the material to 700°C in an electric furnace, after initially placing the sample in a protective tube and creating a vacuum (to 10^{-3} Pa) in the tube, and then performing measurements at the desired temperatures while gradually lowering the temperature in the electric furnace from 700°C to room temperature. Sapphire monocrystal was also /1374
used as a control sample.

2.7 Measurement of High-temperature Hardness and Fracture Toughness Values (K_{Ic})

The resultant samples were parallel ground, afterwhich, their surfaces were mirror-finished using boron carbide grit (#600) and diamond paste (10, 4, 2, 0.3 um).

A Nikon QM Vickers hardness gauge was used in the measurement of microhardness. A vacuum (to 10^{-3} Pa) was created in the testing chamber to prevent the oxidation of the samples and the diamond pressure tip, and the measurements were performed every 100°C from room temperature to 1200°C, using a Vickers diamond pressure tip (200 gram load).

The method used by Niihara, et al. [10] was utilized in the measurement of the fracture toughness of the pre-sintered samples [9], with equipment using a Vickers hardness gauge. K_{Ic} was determined by applying a pressure point load (1 kg) to the samples to develop not only pressure mark, but also cracks, and then reading 1/2 (a) the length of the diagonal lines (2a) of the pressure mark and the length of the cracks (c) extending from each point of the pressure mark using an optical microscope.

3 Results and Observations

3.1 Hot Isostatic Press Sintering of the Glass-encapsulated Materials

The dependency on temperature of the relative density and beta-phase content of SN-A and SN-C powders which were HIP treated for two (2) hours at 1450 to 1700°C and 150 MPa (120 MPa only at 1700°C), with and without additives, is shown in Figure 2. Also, Figure 3 shows the changes in the relative density of sintered samples which were HIP treated for 60 minutes at 1700°C, 120 MPa while changing the amounts of the additives used. The relative densities of the additive-charged Si_3N_4 in these instances is a percentage, obtained by dividing its volume density by the calculated density obtained from the mixture ratio and relative weight of each of the additive ingredients. There is practically no densification 1450°C when additives are present, but as the temperature reaches 1500°C, densification is rapid. However, even if the HIP treatment temperature is raised beyond this, relative density does not increase even much further. Also, since the relative density did not reach even as high as approximately 90% when SN-C was used by itself, it could be said that this is a base material in which densification is difficult. The differences in densification are believed to be related to the relationship between the purity of the base material and the phase transition rate from alpha to beta, due to the differences in the base powders SN-A and SN-C. It was also observed, through the SEM observation of fracture surfaces, that there was

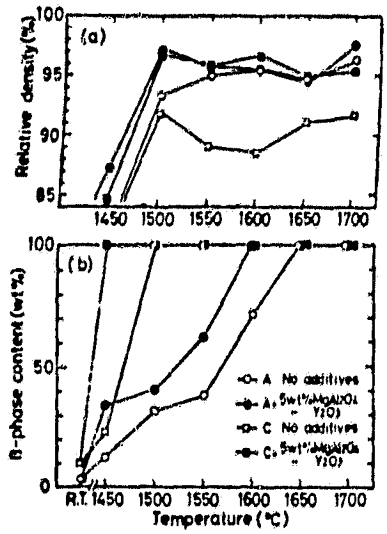

Fig. 2. Effects of temperature on (a) relative density and (b) β-phase content of Si_3N_4 HIP'ed at 150 MPa for 2 hr in Ar gas. The pressure for HIPing at 1 700°C was 120 MPa.

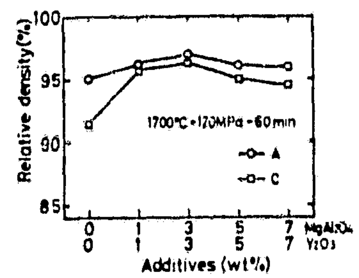

Fig. 3 Relation between relative density and the amount of additives.

veritably no growth in the crystal grains of non-additive-charged materials at 1500°C, but that there was a fair amount of crystal growth in these materials as the temperature reached 1600°C. While, in the additive charged materials, general crystal growth was observed at 1500°C, this tendency being remarkable in the case of SN-A. Also, increasing the additive amounts did not particularly promote densification, but caused irregular grain growth. In order to approach theoretical density, densification must first be nearly completed without causing any grain growth, afterwhich, a uniform structure must be constructed by causing slight, uniform grain growth, and it is therefore believed that it is necessary to use higher temperatures and pressures than the used in the conditions of this experiment.

3.2 HIP Treatment of Pre-sintered Bodies

The results of density measurements on pre-sintered samples, manufactured pressureless sintering SN-B and SN-C charged with sintering additives, HIP treated for 60 minutes at 1700°C and 120 MPa are shown in Figure 4. In order to discover the influence of the atmosphere surrounding the pre-sintered sample, the pre-sintered samples were placed in Si_3N_4 powder, in BN powder, and on top of BN powder, with the method of placing the material in Si_3N_4 powder showing a tendency to increase density somewhat. However, denstities did /1375

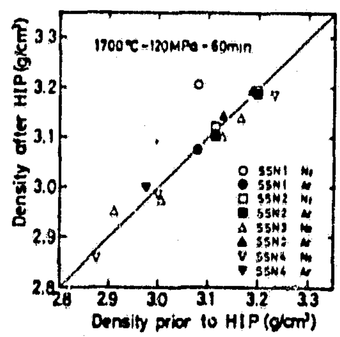

Fig. 4. Effect of HIP treatment on densification.

not change, for the most part, in Ar and N_2 gas HIP treatments either. Only the SSN 1 pre-sintered sample showed a sharp increase in density, from 3.08 to 3.21 grams/cm_2, when HIP treated in N_2 gas. After N_2 gas HIP treatment, this pre-sintered sample had condensed approximately 1 to 2% in length and approximately 3 to 4% in volume, with nearly the same content of closed air pockets as before HIP treatment. It was also observed, from the results of X-ray diffraction analysis, that the Si_3N_4 crystal structure had already already experienced 100% transition to beta-phase in the manufacture of this pre-sintered sample since the sintering temperature had reached as high as 1750°C, making further phase transition through HIP treatment unnecessary. Also, no more than the peak of the beta-Si_3N_4 was observed, even after Ar gas and N_2 gas HIP treatment. Scanning electron micrographs of the fracture surfaces of SSN 1 pre-sintered samples as sintered, and after Ar gas HIP and N_2 gas HIP treatments, are shown in Figure 5. Figure 6 shows the fracture surfaces of SSN 2 pre-sintered samples as sintered and after N_2 gas HIP treatment. It can be seen in Figure 5 that, when Ar gas HIP treated, most of the air pockets in SSN 1 are not lost in

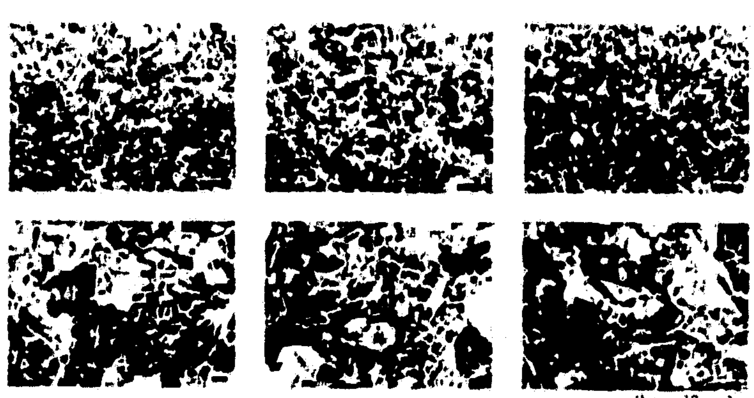

Fig. 5. Scanning electron micrographs of fracture surface (SSN 1).

spite of HIP treatment under 120 MPa high-pressure gas and that their is virtually no visible change in the crystal structure. However, in the case of the N_2 gas HIP treatment, in addition to slight grain growth, most of the air pockets have been eliminated, showing a microstructure that well reflects the results of increased density. On the other hand, in the case of SSN 2, virtually no loss of air pockets can be seen and the structure shows practically no change, in spite of N_2 gas HIP treatment. From this, it is believed that the additives added to the pre-sintered samples have a great effect on the results of HIP treatment.

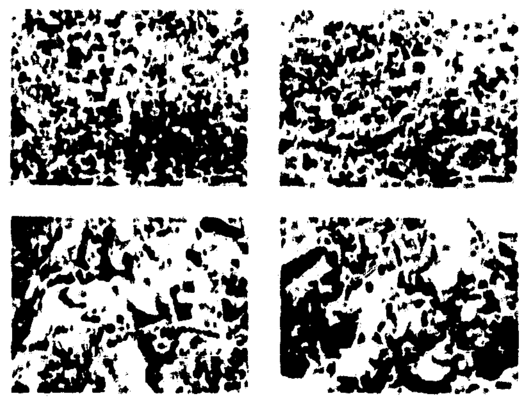

Fig. [illegible] Scanning electron micrographs of fracture surface (SSN 2).

Volumetric expansion was observed in those samples that were Ar and N_2 gas HIP treated. The cause of this not due to the disintegration of the sample surfaces, but was due, instead, to decreases in density through HIP treatment. However, the reasons that the volume of the pre-sintered samples expands through HIP treatment are presently unclear.

3.3 Flexural Strength

The results of the flexural strength measurement of pre-sintered SSN 1 and SSN 2 samples which were subsequently Ar and N_2 gas HIP treated for 60 minutes at 1700°C and 120 MPa in beta-

Si_3N_4 powder, in BN powder, and on top of BN powder are shown in Figure 7. The SSN 2 pre-sintered samples showed a slight increase in flexural strength when HIP treated in beta-Si_3N_4 powder, but was, for the most part, unchanged from the rest of the samples. On the other hand, in the case of the SSN 1 samples, increases were observed in the flexural strength of Ar and N_2 gas HIP treated pre-sintered samples, particularly those treated with N_2HIP, which showed an approximate 50% increase in flexural strength from 330 MPa to 500 MPa. Since beta-phase transition is already 100% and virtually no grain growth is visible in the pre-sintered samples, as explained above, it is believed, from SEM observation, that this increase in flexural strength can be attributed to densification through the elimination of air pockets. Since this increased flexural strength was also seen in those pre-sintered samples which were Ar gas HIP treated, there is also the possibility that densification is slightly promoted in pre-sintered samples which are HIP treated by Ar gas pressure. There is also a tendency in those pre-sintered samples HIP treated in beta-Si_3N_4 powder to have greater density and flexural strength increases due to the elimination of air pockets than those HIP treated in BN powder and on top of BN powder. This indicates that the BN granules and the impurities contained /1376

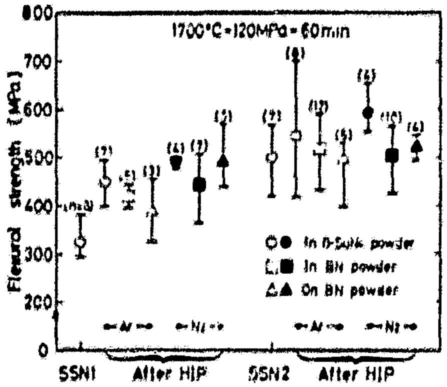

Fig. 7. Room temperature flexural strength. Numerals in ( ) indicate the number of samples tested. The open symbols are for Ar-HIP'ed Si_3N_4 and the filled symbols for N_2-HIP'ed Si_3N_4.

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therein have a detrimental effect on the pre-sintered bodies.

3.4 Thermal Conductivity of Si_3N_4 Sintered Bodies

The thermal conductivity at different temperatures of additive-charged and uncharged SN-A and SN-C samples which were HIP treated for 2 hours at 1700°C and 120 MPa and for 4 hours at 1600°C and 150 MPa are shown in Figure 3. The uncharged samples showed thermal conductivity of 22 to 25 W/mK at room temperature, with little difference between the low-impurity SN-C and SN-A samples. There was also a tendency for the thermal conductivity to decrease as the additives amounts were increased [11].

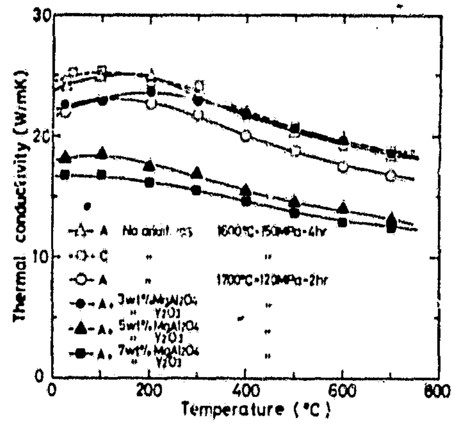

Fig. 8. Temperature dependence of thermal conductivity in Si_3N_4 with and without additives.

The conduction of heat in an insulator such as Si_3N_4 is performed through phonon (nucleon vibration), but as additive amounts increase the grain boundary phase becomes more easily broken by impurities and, consequently, phonon is disrupted and thermal conductivity is decreased. However, when $MgAl_2O_4$ and Y_2O_3 are added simultaneously at 3%wt each, thermal conductivity is practically unchanged from the uncharged samples. The reason for this is believed to be that the disruption to the phonon, due to grain boundary phase, is small when the additive amounts are low, while the growth of the crystal grains, promoted by the additives, contributes to increased thermal conductivity.

3.5 High-temperature Strength and Fracture Toughness (K_{Ic}) of Si_3N_3 Sintered Bodies

Figures 9 and 10 show the dependencies on temperature of the hardness and K_{Ic} of sintering additive-charged and uncharged SN-A samples which were HIP treated for 60 minutes at 1650°C and 150 MPa. Additive-charged samples showed a marked decrease in hardness at around 900°C, which is believed to be due to the softening of the silicate glass of the $MgAl_2O_4$-Y_2O_3 system which surrounded to the grain boundaries [11][12]. On the other hand, the hardness of the uncharged samples showed a much slower decline at around 800°C. This is believed to be attributable to the formation of silicate glass from the SiO_2 in the base material or from ingredients which seeped into the sample from the pyrex glass used as a container in HIP treatment. An Si_2N_2O peak was actually observed by X-ray diffraction analysis in the uncharged samples.

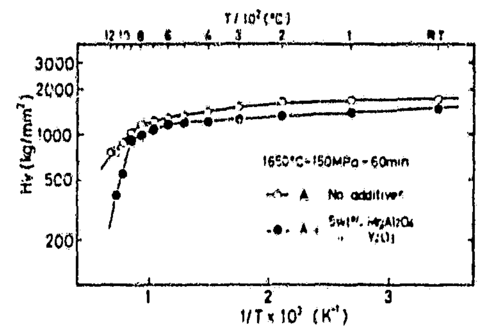

Fig. 9. Temperature dependence of Vickers microhardness of HIP'ed Si_3N_4.

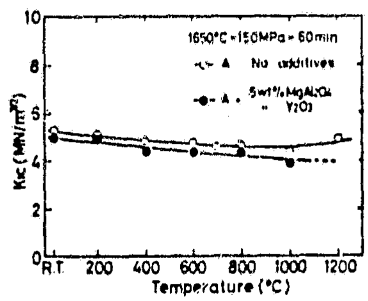

Fig. 10. Temperature dependence of fracture toughness of HIP'ed Si_3N_4.

Meanwhile, both the charged and uncharged Si_3N_4 showed K_{Ic} of approximately $5MN/m^{3/2}$ at room temperature, which gradually decreased as the temperature was increased. In the case of the additive-charged sample, condensation of the additives occurred on the surface of the sample at high temperatures (1200°C) since it was placed in a vacuum and a liquid phase formed, making the measurement of K_{Ic} extremely difficult. Judging from the fact that the pressureless-sintered, additive-charged samples formed liquid-phase at approximately 1200°C, it is believed that perhaps sintering was not completely promoted by HIP treatment and that, consequently the additives were not sintered, but adhered to the grain boundaries simply as impurities.

Figures 11 and 12 the dependencies on temperature of the hardness and K_{Ic} of SSN 1 pre-sintered samples and N_2 gas HIP treated SSN 1 samples. It is apparent through Figure 11 that the hardness increased as much as 200 kg/mm_2 in Vickers hardness after HIP treatment as compared to before HIP treatment. The cause of this is believed to be the fact that air pockets are eliminated and air space, which creates plasticity, was decreased. The dependency of hardness on temperature was virtually the same in the HIP treated and untreated sintered /1377 bodies, in that they both decreased slightly in hardness at around 900°C. HIP treated and untreated samples both also showed K_{Ic} of approximately 5.3 $MN/m^{3/2}$, similar fluctuations even as

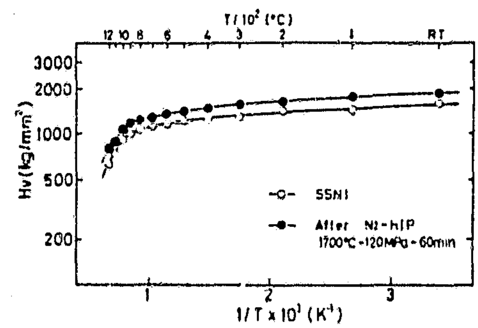

Fig. 11. HIPing effect on Vickers microhardness. The open circle is for the pre-sintered Si_3N_4 (SSN 1) and the filled circle for N_2 HIP'ed body of SSN 1.

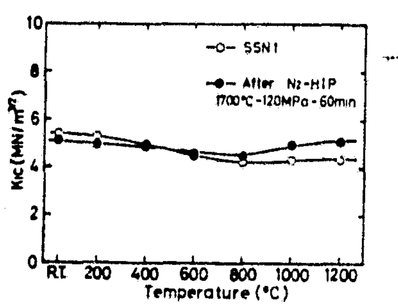

Fig. 12. Temperature dependence of fracture toughness. The open circle is for the pre-sintered Si_3N_4 (SSN 1) and the filled circle for N_2 HIP'ed body of SSN 1.

temperatures were increased, and tendencies for K_{Ic} to increase slightly at over 1000°C, corresponding to the softness of the grain boundaries [12][13][14].

4. Conclusions

Sintered bodies were manufactured in this research by HIP treating additive charged and uncharged Si_3N_4 powders using a glass container, in addition to directly HIP treating Si_3N_4 pre-sintered bodies which had been manufactured by the pressureless sintering method. The relationship between the density of the resultant sintered bodies and additives, in addition to the Vickers hardness, fracture toughness, flexural strength, and thermal conductivity of these sintered bodies, was investigated, yielding the following results.

(1) When glass containers were used, hardness was easily increased to approximately 95 to 96% of theoretical density, but theoretical hardness of greater than this not attained in spite of increased temperature conditions and increased additive amounts.

Meanwhile, in the case of the pre-sintered materials, the manufacture of pre-sintered bodies corresponding to the HIP conditions is an extremely important process, and it is believed that theoretical density can be attained simply producing pre-sintered bodies which correspond to the HIP treatment.

(2) It is believed that the increased flexural strength through the HIP treatment of the pre-sintered bodies resultant from this research was due to the elimination of air pockets, a

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cause of the formation of cracks, rather than the structural change from alpha-phase to beta-phase. The increase in flexural strength due to HIP treatment was approximately 50%. It was also discovered that HIP treatment in beta-Si_3N_4 powder is better than other methods.

(3) The thermal conductivity of Si_3N_4 without additives was shown to be approximately 22 to 25 W/mK at room temperature through HIP treatment, which decreased as the additive amounts were increased.

(4) The fracture toughness value of additive-charged and uncharged Si_3N_4, HIP treated using a glass capsule, was shown to be approximately 5 $MN/m^{3/2}$.

(5) IN the case of the HIP treatment of pre-sintered bodies, the density, flexural strength, and hardness of SSN 1 was increased remarkably by N_2 gas HIP treatment, but there was little change in its fracture toughness value.

(From a December 5, 1983 lecture at the 13th Ceramic Materials Committee Meeting (Dai 13-kai Seramikkusu Zairyō Bumon I-inkai)

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